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13. ABSTRACT *(Maximum 200 words)*

The program focus is to create new optical sensors based on bio-inspired concepts and use them for sensing applications of relevance to the United States Air Force, especially for applications in the micro- and nano- domains. This proposal seeks to unite the areas of optical chemo/bio-sensing (CB sensing) and nanoscience. As the advancement of chemical sensing systems progresses towards small length scales, sensitivity and performance are comprised because there are simply too few sensing active sites on the micro- and nano-patterned structures to permit detection of species. Accordingly, this proposal seeks to develop strategies to increase CBsensor response by replacing the linear, single photon response of present sensors with extremely nonlinear optical responses. To achieve this objective, a multi-prong approach that combines materials chemistry, engineering and optical science is presented in which the light emitting molecular centers of conventional optical chemosensors are substituted with a mesoscopic optical laser cavity of a Distributed Feedback (DFB) structures and spherical cavity resonators exhibiting Whispering Gallery Modes (WGM). By tuning the frequency of the resonator to a specific property of the target biomolecule, the laser response can be interrupted upon recognition of the target at the surface of the resonator. In this way, a large change in nonlinear laser signal is easily detected upon target recognition.

By uniting optical chemosensing with nanoscience, we hope to open new avenues to the creation of microsensors possessing unprecedented performance capabilities. As recent events in this Nation highlight, there is a need for detection and quantification of biological and chemical reagents for each person in the civilian and military population. The techniques and principles developed here can be applied to target the many problems in microsensor development and materials applications for the exquisite detection of small concentrations of analyte on small length scales.

14. SUBJECT TERMS
Bio-inspired sensors, whispering gallery mode, distributed feedback structures, nanolasers, high gain sensing, quantum dots, nanocrystal semiconductors, slab waveguide, aircraft design, chem- bio- warfare agents, tempreature sensitive paints, wind tunnel testing, fluid flow diagnostics, bioconjugates

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1. Objectives

The progress report was submitted in September 2004. The final report for the 1-yr project ends on April 2005. Thus the overall objectives, status of effort, accomplishments and other materials were largely covered in the 1-yr progress report for the 1-yr grant. The 1-yr progress report is modified below to reflect new additions over the short period between progress and final reports. The program objective is to create new optical sensors based on bio-inspired concepts and use them for sensing applications of relevance to the United States Air Force – from the detection of chem-/bio- warfare agents to sensing physical processes needed for the design of high performance jet aircraft.

2. Status of Effort

To achieve the foregoing objective, we have taken an approach that combines synthesis, materials science and fluid engineering. The synthesis prong of our attack is concerned with the design of optical supra-molecules and materials that operate on the principles of bio-recognition. A luminescent signal is produced upon the recognition of the target, allowing us to construct the first microfluidic optical chemo- and bio-sensors (CBsensors). The miniaturization offered by these devices allows species to be detected at trace concentrations, in minute volumes and with high fidelity and offers the possibility for massive parallelism, opening the door to the development of widely distributed sensing networks for a variety of U.S. Air Force applications (see Transitions Section 6.3.2).

Our studies of small-scale devices, however, have revealed a shortcoming – as the size of sensors moves toward micro- and nano-dimensions, the sensitivity of the device is compromised because there are simply too few sensing active sites. We see this issue as the fundamental challenge confronting the design of CBsensors on the nanodomain. To address this challenge, we are currently developing and fabricating: (i) new materials and transduction mechanisms that will amplify the primary optical signal from the CBsensing active site in micro- and nano-environments and (ii) new sensing elements and devices to achieve high gain from a non-linear optical response. The payoff of our approach will be the creation of microsensors possessing unprecedented performance capabilities.

3.1. Accomplishments/New Findings

Our previous work has led us to the inexorable conclusion that the integration of nanoscience with CBsensing will require new signal transduction strategies. As the advancement of chemical sensing systems progresses towards small length scales, sensitivity and performance are compromised because there are simply too few sensing active sites on the micro- and nano-patterned structures to permit detection of species. This is especially pertinent to the new bio-inspired sensing mechanism that we invented in this AFOSR program – the 3R (recognize, relay, report) signaling scheme. The approach is now widely accepted and used by many in the field of optical sensing. In this scheme, an analyte binds at a recognition site, thus triggering a single photon emission at the reporter site. We find that this *single*

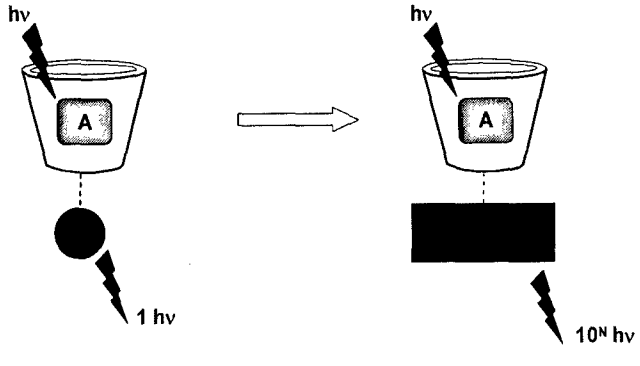


Figure 1. *New design concept for 3R CBsensing that was achieved during past project period. A single photon emitting center is replaced by a laser, which can be turned off or on by the recognition of a target. The approach allows for high gain responses, even in the presence of very few target molecules.*

molecule detection – single photon generation strategy, however, yields signals too weak to be detected on small length scales. We have therefore sought alternative strategies to increase sensitivity by replacing the linear, single photon response of present CBsensors with an extremely nonlinear optical response. To

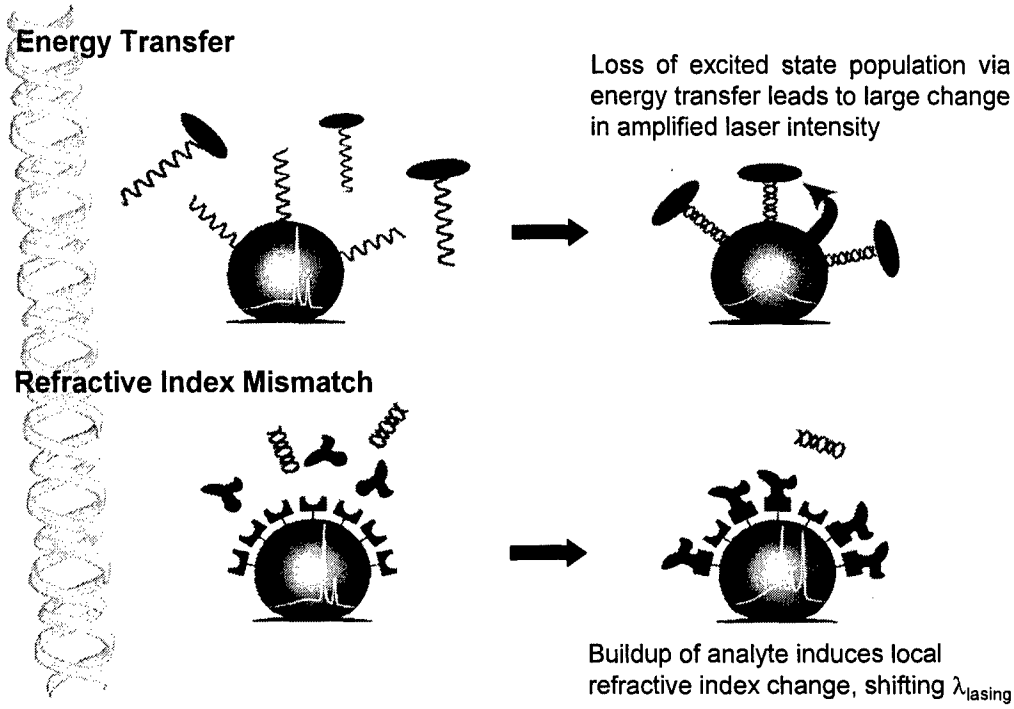


Figure 2. *Two possible sensing strategies for spherical laser cavities adapted with bio-recognition sites for high gain sensing of target biomolecules.*

achieve this objective, we have replaced the emission centers of our 3R CBsensor design with the high gain response of a laser cavity. The approach is schematically represented in Figure 1.

Lasing from the cavity is turned off and on by the presence of an analyte. We therefore increase the signal response from a single photon to 10^N photons where N is a very large number. Because laser signals are easy to detect, a response can be observed in the presence of very few target molecules that one wishes to detect.

The approach allows the sensing strategies in Figure 2 to be established with facility. In one case, recognition of a target molecule introduces a new loss mechanism by interfering (either by absorption or energy transfer) with the propagating lasing wavelength. When the loss of the laser cavity is greater than the gain, the laser will turn off, which is easily observed. In the other strategy, a very narrow laser line is shifted in wavelength upon recognition of the target biomolecule because the lasing wavelength is very sensitive to the refractive index of the gain medium. If the laser lines are sufficiently narrow, adsorption of the biomolecule at the surface will alter the index of refraction sufficiently to shift the lasing wavelength.

The past project period has focused on building small-scale laser cavities with optical properties to enable high gain sensing. We have fabricated three types of nanolasers: (1) a Distributed Feedback (DFB)

structures, based on a slab waveguide architecture; (2) micron-sized spheres that lase via whispering gallery modes (WGM) and (3) a microfludic laser. Our work has been a striking success. Fabrication of these lasing architectures provides the prospect of delivering the vast science of optical sensors to the area of nanoscience – opening new avenues for distributed sensor networks that addresses a number of problems currently confronting the US Air Force – from processes of corrosion and the detection of CB warfare agents to physical processes including engineering measurements needed for the design of high performance aircraft.

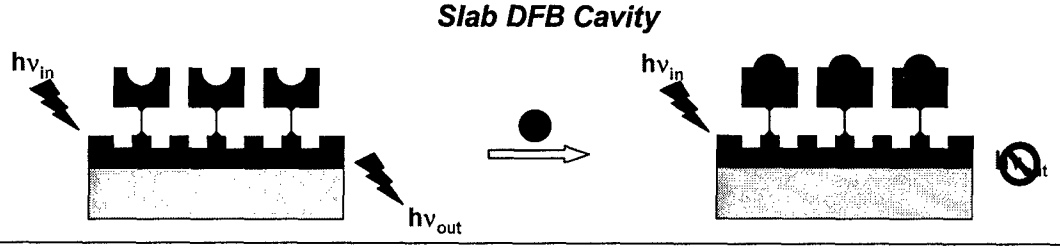


Figure 3. *Sensing with a Distributed Feedback Grating laser modified with bio-recognition sites (aqua rectangle) for target biomolecule (red ball). The cavity on the left is lasing. When the biomolecule binds, it introduces a loss mechanism thereby turning the microlaser off (as depicted on the right).*

3.1.1. Distributed Feedback (DFB) Structures as Laser Cavities for High Gain Sensing

The intensity of light can build exponentially as a beam propagates in a cavity with an inverted population. This increase in intensity, or gain, is given by,

$$I = I_0 e^{g(\nu)\cdot x} \tag{1}$$

where I_0 is the impinging intensity, I is the intensity at position x in the cavity and $g(\nu)$ is the gain coefficient given by,

$$g(\nu) = [N_e B_e(\nu) - N_g B_g(\nu)]\frac{h\nu}{c} \tag{2}$$

$N_{e(g)}$ is the number of excited (ground) state population and $B_{e(g)}(\nu)$ is the emission (absorption) probability at frequency ν. The removal ("turn-off") or addition ("turn-on") of energy to the cavity will affect the gain coefficient and thus have an exponential effect on the laser output. We wish to affect the gain coefficient by chemically functionalizing the laser structures with bio-recognition sites (see Figure 3). Absorption of the propagating light by the target biomolecule recognized by the bioreceptor site will turn the laser off if the gain drops below the threshold needed for lasing action within the cavity. The exponential gain in intensity and narrow emission linewidth associated with lasing will no longer be observed if the population inversion necessary for laser amplification is not obtained. In this way, an exponential response to a target analyte may be achieved, thus providing us with a non-linear response to achieve exquisite sensitivity on extremely small length scales.

We have begun exploring the use of a distributed feedback (DFB) grating for the lasing reporter site shown in Figure 3. Feedback necessary for laser operation is typically provided in a laser oscillator by a mirror at each end of the cavity. Appropriate boundary conditions on standing waves result in the formation of discrete longitudinal modes. A DFB grating has numerous such cavities, created by embossing a grating on a waveguide. As a propagating wave traverses the grating, the electric field

intensifies by the constructive (and destructive) interference of light from each cavity. Lasing builds up if the grating period Λ satisfies the Bragg condition,

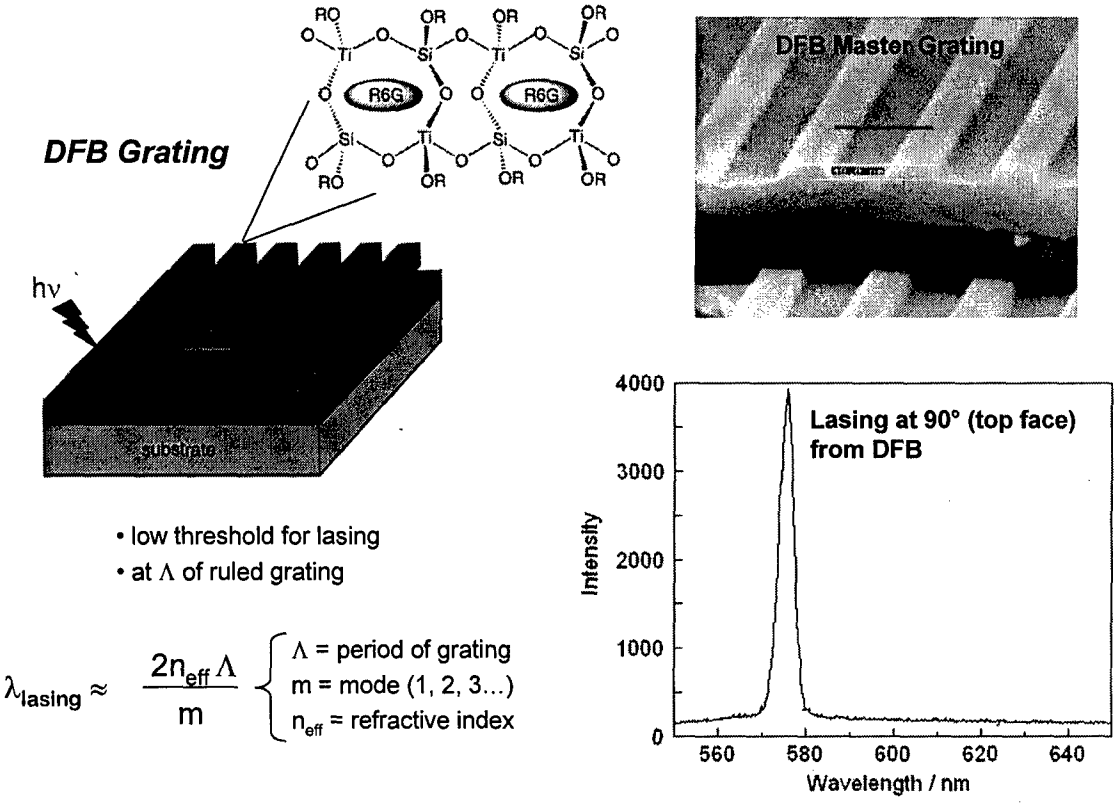


Figure 4. *(Left) Schematic of the DFB architecture showing the molecular framework of the TiO_2/SiO_2 medium incorporating a laser dye, Rhodamine 6G (R6G). (Upper right) SEM of the master grating fabricated by using interference lithography in the Research Laboratory of Electronics at MIT. The master grating can be preserved by subsequent transfer to a poly(dimethylsiloxane) (PDMS) stamp. A second order, DFB lasing structure is obtained by stamping the PDMS onto a freshly spin-coated thin film of the TiO_2/SiO_2 slab waveguide. (Lower right) Lasing obtained from fabricated DFB.*

$$\Lambda = \frac{\lambda_B m}{2n_{eff}} \tag{3}$$

where λ_B is the Bragg wavelength, m is the order of the grating reflection, and n_{eff} is the effective refractive index. From eq. (3), we see that the lasing medium must have a gain profile that overlaps with λ_B. The resulting laser emission has very narrow linewidths and high wavelength selectivity. We have prepared the DFB architecture shown in Figure 4 by accomplishing the following research during the funding cycle:

- synthesized a slab waveguide medium prepared from a TiO_2/SiO_2 sol-gel matrix
- determined synthesis conditions to yield the medium possessing proper refractive index and smoothness to exhibit waveguide properties
- incorporated laser dyes into the slab waveguide medium so that the amplified stimulated response needed for lasing could be established; Figure 4 (left panel) shows a schematic of the silica/titania framework of the slab waveguide including Rhodamine 6G
- fabricated master grating (upper right panel of Figure 4) in the Research Laboratory of Electronics at MIT by using interference lithography; the grating stamp has a period of Λ to satisfy the condition of eq. (3)
- transferred master grating pattern onto PDMS stamp, which was used to produce the imprinted grating on the slab waveguide, schematically represented in the left panel of Figure 4
- characterized DFB optical properties
- observed lasing from DFB architecture, depicted in the lower right panel of Figure 4

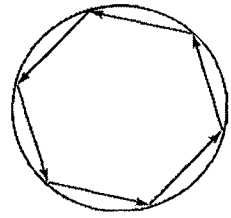


Figure 5. *WGMs are formed from successive internal reflections inside a spherical cavity.*

3.1.2. Spherical Nanolasers based on Whispering Gallery Mode (WGM) Resonance

Laser emission in spherical resonators is the result of light trapping in the so-called WGMs, which are formed from successive total internal reflections off the concave inner surface as depicted in Figure 5. As light propagates in this fashion, the photonic electric field strength increases exponentially as a result of

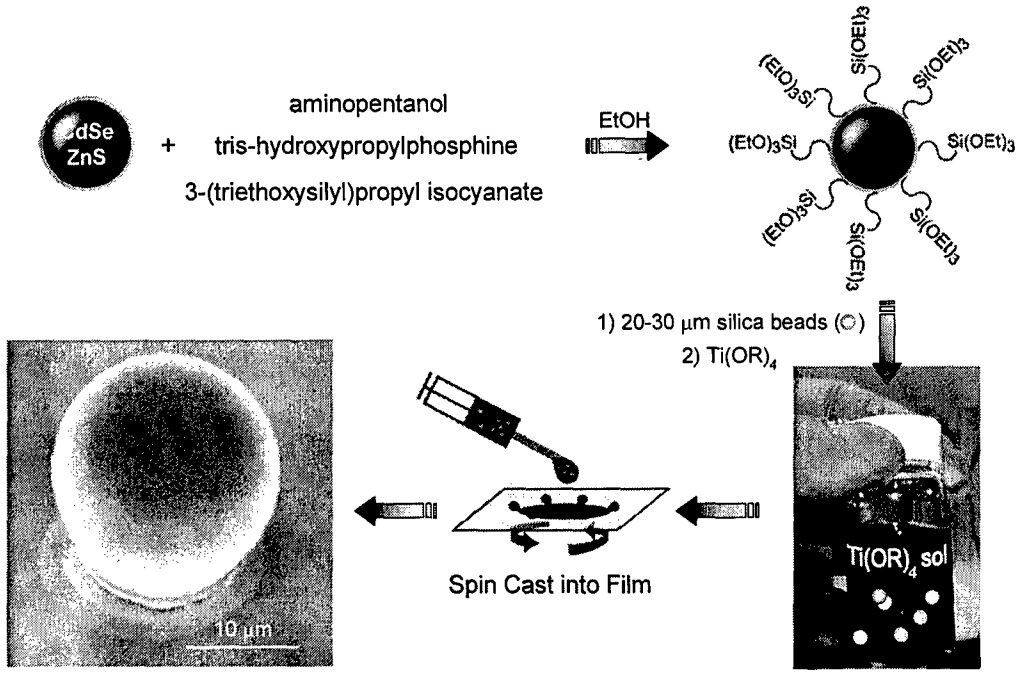


Figure 6. *Our patented process for making WGM lasers with CdSe nanocrystals as the gain material. An SEM micrograph of a microsphere is shown.*

stimulated emission from an inverted population of a suitable laser gain material. The laser quality Q factor of these modes can be extremely high because of the strong confinement of photons within the modal volume. However, it is difficult to incorporate a laser gain material into a high quality spherical cavity. Previously established methods of producing WGM microsphere resonators rely on the use of organic laser dyes which are known to quickly and irreversibly photobleach. We have overcome this problem by using semiconductor nanocrystals (NCs), which are much more resilient under optical excitation compared to organic laser dyes. Furthermore, the NC surface may be chemically functionalized to support adhesion onto the exterior of a microcavity, such as a silica or polystyrene microsphere. Thus, a non-linear sensing scheme based upon spherical resonant cavities employing a NC gain material is particularly attractive. We have developed a facile and robust method of incorporating colloidally synthesized CdSe/CdZnS NCs onto the surface of micron-sized silica or polystyrene microspheres by depositing a NC/titania or silica sol onto the microsphere substrate, producing hundreds of uniform spherical resonators in a single spin-coating process as summarized in Figure 6. The method has been

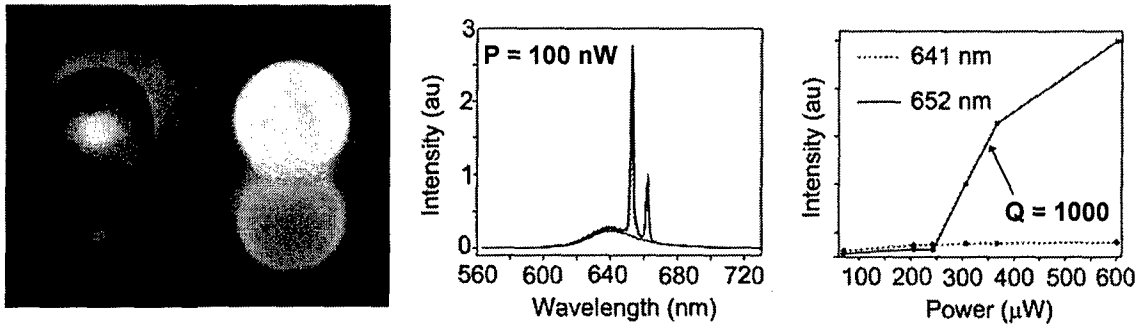


Figure 7. *(Left) A 20-micron CdSe/microsphere begins lasing upon pumping the CdSe NC emission. (Middle) Amplified Stimulated Emission (ASE) fluorescence from the CdSe (bottom trace) transforms into discrete, sharp optical resonances once the lasing threshold is crossed. (Right) Power response of the CdSe NC emission intensity, on and off resonance. The off resonance threshold shows a linear response whereas the on resonance shows a highly nonlinear increase in intensity at a threshold pump intensity. The Q factor for the spherical laser cavity is extremely high.*

patented owing to the remarkable optical properties of spheres obtained by this method.

Stable room temperature Whispering Gallery mode (WGM) laser emission from these structures has been observed using a home-built imaging/dispersive fluorescence microscope coupled to a frequency doubled 1 kHz Ti:sapphire regeneratively amplified laser light source for pumping the devices. The lasing response and optical characteristics of the CdSe/microspheres are shown in Figure 7. Simultaneous lasing from both biexcitonic (shown) and multiexcitonic (not shown) states has also been demonstrated. Single mode versus multimode lasing can be selectively achieved by adjusting the size of the microsphere template, spectral position of the gain of the NC sample, and the pump power of the laser. Our microsphere resonators are also very stable over time. Furthermore, laser emission has been observed to recover partially if a photobleached sample is left in the dark for several minutes, similar to previous observations made in fluorescence quenching studies of CdSe NCs. We have also demonstrated lasing when the sample was immersed in a liquid such as ethanol or water, which makes these structures suitable for CBsensing applications. Our method is general as we have recently achieved blue lasing from CdS/ZnS NCs as the gain material.

3.1.3. Future Plans

With the spectacular results of Figure 6 in hand, we are now posed to implement the CBsensing strategy depicted in Figure 2. Pending the availability of funds, bio-conjugates may be introduced onto the surfaces of DFB and WGM resonators, thus providing a receptor site for target biomolecules. Our work has placed us on the doorstep of creating CBsensors using bio-inspired concepts that possess unprecedented performance capabilities.

4. Personnel

A graduate student and a postdoctoral associate has performed the chemistry, materials science, and optical and laser spectroscopy during the past year. Ms. *Aetna W. Wun*, who hails from the University of California at San Diego, is a fourth-year graduate student who has stepped into the position vacated by Christina Rudzinski (see Section 6.3). Aetna is well versed in chemical and materials synthesis. She complements this expertise with a sound knowledge of optics and laser spectroscopy. She is responsible for the continued development of DFB architectures for nanosensing. Dr. *Preston Snee* graduated from U. C. Berkeley (Ph.D., Physical Chemistry, 2002). He is an expert laser spectroscopist and is spearheading the development of WGM resonators for this project. Ms. *Becky Somers*, who hails from Northwestern, joined the project this year as a first year graduate student. She is using the high gain resonators to perform bio-sensor applications.

5. Publications

1. "Whispering Gallery Mode Lasing from a Semiconductor Nanocrystal/Microsphere Resonator Composite"; Preston Snee, YinThai Chan, Daniel G. Nocera and Moungi G. Bawendi, *Adv. Mater.* **2005**, *17*, 1131-6.

2. "Blue Semiconductor Nanocrystal Lasers"; YinThai Chan, Jonathan S. Steckel, Preston T. Snee, Jean-Michel Caruge, Justin M. Hodgkiss, Daniel G. Nocera and Moungi G. Bawendi, *Appl. Phys. Lett.* **2005**, *86*, 073102/1-2.

3. "Non-linear Transduction Strategies for Chem-/Bio- Sensing on the Nanoscale"; Aetna W. Wun, Preston T. Snee, YinThai Chan, Moungi G. Bawendi and Daniel G. Nocera, *J. Mater. Chem.* **2005**, *Fluorescent Sensors* special issue, (Advanced Article), DOI: 10.1039/b503026a.

4. "A Low-Threshold, High-Efficiency Microfluidic Waveguide Laser"; Dmitri V. Vezenov, Brian T. Mayers, Richard Conroy, George M. Whitesides, Preston Snee, Yinthai Chan, Daniel G. Nocera, and Moungi G. Bawendi, *J. Am. Chem. Soc.* **2005**,*12* , 8952-3.

5. "Structural Tuning of a Ligand-Based Two-Electron Intervalence Charge Transfer"; Julien Bachmann and Daniel G. Nocera, *Inorg. Chem.* **2005**, submitted for publication.

6. "Single Quantum Dot (QD) Imaging of Fluid Flow Near Surfaces"; Shahram Pouya, Manoochehr Koochesfahani, Preston Snee, Moungi Bawendi and Daniel Nocera, *Exp. Fluids* **2005**, accepted for publication.

7. "Molecular Tagging Velocimetry"; Manoochehr M. Koochesfahani and Daniel G. Nocera, Springer-Verlag, **2005**, submitted for publication.

8. "$[Ru(4,7\text{-diphenyl-}1,10\text{-phenanthroline})_3]Cl_2$"; Glen W. Walker and Daniel G. Nocera, *Inorg. Synth.* **2004**, *34*, 66-68.

9. "Excited-State Distortion of Rhenium(III) Sulfide and Selenide Clusters"; Thomas G. Gray, Christina M. Rudzinski, Emily E. Meyer and Daniel G. Nocera, *J. Phys. Chem. A* **2004**, *108*, 3238-3243.

10. "Spectroscopic and Photophysical Properties of Hexanuclear Rhenium(III) Chalcogenide Clusters"; Thomas G. Gray, Christina M. Rudzinski, Emily E. Meyer, R. H. Holm and Daniel G. Nocera, *J. Am. Chem. Soc.* **2003**, *125*, 4755-4770.

11. "Quantum dot optical temperature probes"; Glen W. Walker, Vikram C. Sundar, Christina M. Rudzinski, Moungi G. Bawendi and Daniel G. Nocera, *Appl. Phys. Lett.* **2003**, *83*, 3555-3557.

6. Interactions/Transitions

6.1. Presentations

6.1.1. Popular Press

The PI was the feature of an ABC Nightline with Ted Koppel: "Little Black Box", 25 August 2003. The show highlighted recent research advances from the Nocera group.

In addition, the Nocera research program was the focus of a pilot film for a new PBS show, called the *ScienceNow,* produced by NOVA. The producers of NOVA wished to create a new show that educates the public about the fundamental science that precedes major discovery. The pilot was produced as a fund raiser for this new show and generated in over $10 million. It is targeted to educate but also be fun and informative. This contribution/interaction by the PI will have a lasting impact...a new science program for the public. He will be appearing on the 27 July 2005 show, with a focus on the contributions of his research program.

Finally, our AFOSR-sponsored work has appeared on the front of the MIT webpage and featured in the 2004 Special Edition of *Technology Review*.

6.1.2. Invited Talks only. A list of invited talks for 2004 and 2005:

Harvard University (Department of Chemistry); Cambridge, MA; 9 January 2004.

MRS/MIT Lecture (Department of Materials Science and Engineering); Cambridge, MA; 15 January 2004.

University of Minnesota (Department of Chemistry); Minneapolis, MN; 6 February 2004.

Michigan State University (Department of Chemistry); East Lansing, MI; 18 February 2004.

Florida State University (Department of Chemistry, Organic Seminar Series); Tallahassee, FL; 26 February 2004.

Florida State University (Department of Chemistry, Colloquium); Tallahassee, FL; 27 February 2004.

Georgia Institute of Technology (Department of Chemistry); Atlanta, GA; 2 March 2004.

Iowa State University (Department of Chemistry); Ames, IA; 12 March 2004.

Colorado State University (Department of Chemistry); Fort Collins, CO; 15 April 2004.

University of Colorado (Department of Chemistry); Boulder, CO; 16 April 2004.

AFOSR/ONR Electrochemistry Review; Annapolis, MD; 19-20 April 2004.

Uppsala University (Department of Chemistry); Uppsala, Sweden, 21 April 2004.

Uppsala University (Institute of Artificial Photosynthesis); Uppsala, Sweden, 21 April 2004

Stockholm University (Department of Chemistry); Stockholm, Sweden, 23 April 2004.

Boston College (Department of Chemistry); Chestnut Hill, Boston, 7 May 2004.

Ford Motor Company, Dearborn, Michigan, 25 May 2004.

Cummins Inc.; Columbus, Indiana, 23 June 2004.

Plenary Lecturer; 15th International Symposium on the Photochemistry of Coordination Compounds; Hong Kong, China; 3-9 July 2004.

Invited Lecturer; International Conference of Porphyrins and Phthalocyanines; New Orleans, LA; 11-16 July 2004.

Plenary Lecturer; 36th International Conference on Coordination Compounds; Merida, Mexico; 18-23 July 2004.

Repligen Award Symposium; 228th American Chemical Society; Philadelphia, PA; 22 - 26 August 2004

Lincoln Laboratory (Biodefense Systems); Lexington, MA 10 September 2004

Fackler Symposium; 60th Southwest ACS Regional Meeting; Fort Worth, TX; September 29 - October 2, 2004

Terrascope Seminar, Massachusetts Institute of Technology (Earth Systems Initiative); 19 October 2004.

Massachusetts Institute of Technology (Laboratory for Energy and the Environment); Cambridge, MA; 1 December 2004.

NSF Distinguished Lecturer, National Science Foundation, Washington, DC, 14 December 2004.

Georgetown University (Department of Chemistry); Washington, DC, 15 December 2004.

Plenary Speaker, 5th Boston Regional Inorganic Colloquium, Tufts University; 19 February 2005.

Plenary Lecture, Scientific Research and the Future of Energy; University of Venice; 2 March 2005.

Italgas Prize Lecture, University of Turin: Turin, Italy; 4 March 2005.

Sacconi Lecturer, University of Florence; Florence, Italy; 7 March 2005.

AFOSR/ONR Electrochemistry Review; Annapolis, MD; 23 March 2005.

University of Pennsylvania (Department of Chemistry); Philadelphia, PA; 29 March 2005.

University of Texas at Austin (Department of Chemistry); Austin, TX; 5 April 2005.

Department of Energy, 18 - 21 April 2005.

Plenary Lecture (via videoconference), Re-Establishing Energy: Sustainability Beyond Kyoto, Accademia Nazionale dei Lincei and Accademia Nazionale delle Scienze (XL) and EniTecnologie; Rome, Italy; 26 - 27 April 2005.

University of California at Santa Barbara (Department of Chemistry); Santa Barbara, CA; 2 May 2005.

Italgas Prize Lecture, MIT (Laboratory for Energy and the Environment); Cambridge, MA, 10 May 2005.

Phillips Lecturer, University of Pittsburgh (Department of Chemistry); Pittsburgh, PA, 11-13 May 2005.

16th International Symposium on the Photochemistry of Coordination Compounds; Asilomar, CA; 2-7 July 2005.

6.2. Consultative or Advisory Function

Co-chair, Basic Research Needs for Effective Solar Energy Utilization Department of Energy, Washington, D.C., April 18-21, 2005

Member, President's Energy Research Council, MIT, 2005-present

Organizer and Chair, Collaborative Research in Chemistry Conference; Washington, DC; 2-4 November 2004.

Board of Editors, *Accounts of Chemical Research*, 2001-2003

Board of Editors, *Journal of the American Chemical Society*, 2005-present

Board of Editors, *Inorganic Chemistry*, 2005-present

Board of Editors, *Comments in Inorganic Chemistry*, 2005-present

Scientific Advisory Board, IDP, Polaroid Subsidiary, 2002- present

Member, Provost Task Force for Faculty Quality of Life at MIT, 2003- present

Member, Chancellor Council on the Environment, MIT, 2003-present

Rubin and Anders Associates, 2004-present

6.3. Transitions

Transitions of F49620-01-1-0118 contribute in both technical and human resource arenas.

6.3.1. Human Resource

Dr. *Christina Rudzinski* graduated from FA9550-04-1-02693 and joined the DOD project team on Biological Warfare Defense, which is supported by the US Air Force, US Army, DARPA, Joint Program Office for Biological Defense and the Office of the Secretary of Defense. She is currently the lead scientist on a research project to develop new sensors for biological warfare agents. She was hired at Lincoln Labs because of her expertise in synthesis, photophysics, microfluidics and CBsensor design. These areas of expertise were developed during her graduate work, under the auspices of FA9550-04-1-02693.

6.3.2. Technical

The knowledge gained from our studies will broadly impact the AFOSR. Recent events in this Nation highlight the need for the detection and quantification of biological and chemical reagents for each person in the civilian and military population. Our work provides the underpinning to develop technologies that address this need (e.g. "wristwatch" sensors). We expect to obtain microsensors possessing unprecedented performance capabilities.

We see the transfer of the tools developed in this program to other AFOSR fields as an important benefit of the proposed work. Two examples come to the fore. The methods developed in this program will allow for the invention of new optical diagnostic tools for mapping chemical and physical processes in micro- and nano-domains especially in small channels and near surfaces. Thus liquid/solid interfaces may be examined to allow insights to be gained in disparate areas ranging from corrosion to studies of flow within the cell. Also, the methods developed here provide amplification of signals (especially optical) emanating from signal transducers patterned on small length scales. Thus we see the work described here as the linchpin between AFOSR nanoscience programs, emphasizing architectural development (e.g., DPN) and real world sensing applications. Some of these are highlighted below.

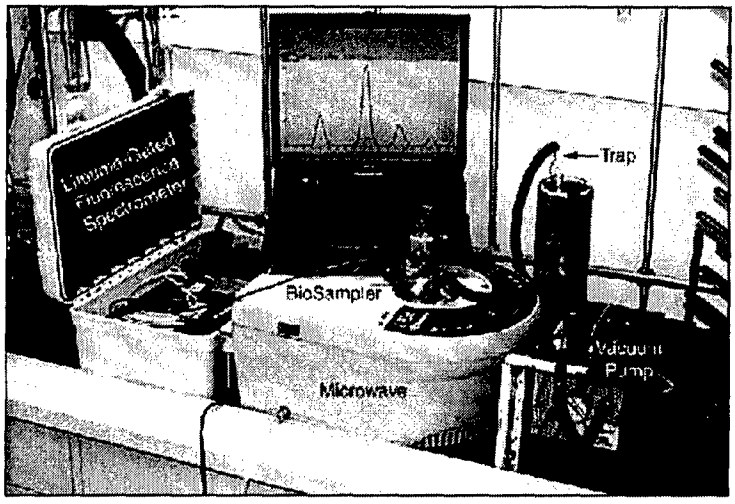
6.3.2.1. An Anthrax Smoke Detector

The anthrax attacks of 2001 highlighted the need for new methods of detecting bioaerosols, especially airborne spores that carry anthrax (*Bacillus anthracis*). Current methods of bacterial spore (endospore) detection, such as colony counting and PCR, require trained personnel for sampling and analysis. Early warning detection systems are needed that are cheap, low maintenance and able to continually monitor

while unattended. In response to this need, a 3R sensing strategy based on Tb^{3+} luminescence has been transitioned to JPL for the development of an anthrax "smoke detector" (ASD). A former student from this AFOSR-sponsored research program and now a staff scientist at JPL, Dr. Adrian Ponce, has implemented the 3R Tb^{3+}-based sensing scheme to design, develop and test an ASD instrument capable of automated monitoring for airborne bacterial spores containing the anthrax bacteria.

The principle of operation of the ASD targets a unique chemical marker, DPA (2,6-pyridine dicarboxylic acid), contained within bacterial spores at high concentrations. When DPA is released into bulk solution by physical (microwave) lysing, it binds terbium ions with high affinity to set up the 3R energy cascade. An intense green luminescence is triggered under UV excitation, thus signaling the presence of bacterial spores. The intensity of the luminescence can be correlated to the number of endospores per milliliter. Concentrations below 100 spores/liter of air trigger a response from the smoke detector in half the time it takes for a person to breathe in a lethal dose of anthrax spores. The ASD thus provides a simple and robust early warning system for the automated, continuous, long-term monitoring instrument of airborne anthrax spores.

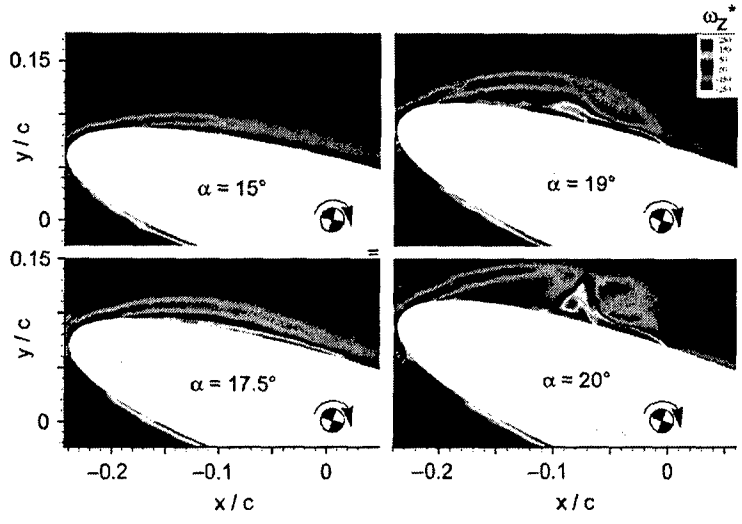
The sensitivity of the ASD is primarily governed by the Tb^{3+}-DPA binding constant, which can be increased by the design and implementation of new Tb^{3+}-based receptor sites that exhibit cooperative binding towards DPA. This work will continue to be performed as a natural outgrowth of this AFOSR program. These new constructs will be transitioned from the laboratory bench of the PI's program to Ponce at JPL, who will incorporate them in next generation ASD prototypes.



The anthrax 'smoke detector' developed at JPL allows for the automated and continuous monitoring of anthrax spores. The operation of the instrument is based on the 3R optical detection scheme developed in FA9550-04-1-02693.

6.3.2.2. Nanocrystal TSP Transition to Wright Patterson Labs

The significant temperature dependence of the luminescence combined with its insensitivity to quenching by oxygen establishes these (CdSe)ZnS-based NC materials as an attractive new class of optical indicators for luminescence thermometry applications. The NC-based technology was directly passed from this AFOSR program to the Aerodynamics Configuration Branch (AFRL/VAAA) of the Air Vehicles Directorate at Wright Patterson Air Force Base for testing and evaluation. This transition was made possible by an STTR involving Innovative Scientific Solutions, Inc. (ISSI), a sub-contractor to the Air Force. All expectations of the NCs as temperature probes were confirmed at Air Force facilities in 6.2 tests. The results of this work have been described in a recent joint publication from the PI labs, AFOSR and ISSI. The intent is to commercialize these temperature-sensitive paints containing (CdSe)ZnS NCs in a 6.3 venture at Arnold and Wright Patterson AFB over the next two years.



Evolution of the vorticity field as measured by MTV at the onset of leading edge separation on an airfoil pitching at high angles of attack. The color scale indicates the quantitative magnitude of vorticity. Purple indicates the most intense clockwise flow and red indicates the most intense counterclockwise flow.

6.3.2.3. Design of Safer and Higher Performance Aircraft for the US Air Force

We have invented the Molecular Tagging Velocimetry or MTV technique, which senses the velocity flow fields of highly three-dimensional turbulent flows, to investigate problems that previously were elusive to the Air Force. One especially important problem under investigation is the flow at the leading edge of an airfoil as its attack angle is increased. It was known by the Air Force that perturbation of the flow at this leading edge upon rotation causes turbulence, the flow detaches and lift is lost. This problem was uniquely addressed by the MTV technique owing to its ability to probe the high three-dimensional character of the flow at a large range of spatial and temporal scales. The project is leading to a better understanding of the conditions for which turbulence at the leading edge is minimized and therefore provides insight into the design of safer and higher performance aircraft.

The rotating airfoil experiment was undertaken in the AFOSR Engineering Directorate (AFOSR F49620-95-1-0391; Koochesfahani, PI). The experiment was computationally examined at Wright Patterson Labs in a joint collaboration with Dr. Miguel Visbal of the Aeromechanics Division, Wright Labs Flight Dynamics Directorate. The work is now part of design efforts at Wright Patterson Labs.

7. New Discoveries, Inventions, Patent Disclosures

"Temperature-Sensing Composition"; Alfred A. Barney, Moungi G. Bawendi, Vikram Chandrasekar Sundar, Daniel G. Nocera, Christina M. Rudzinski and Glen W. Walker, Application filed by MIT on 9 February 2001 (serial number 09/779,437); MIT Internal Case #8800 (2001). U.S. Pat. Appl. Publ. 2002110180 (2002), 9 pp.

"Two Electron Mixed Valence Complexes for Photocatalytic Hydrogen Production"; Alan F. Heyduk and Daniel G. Nocera; Patent Application filed by MIT on 26 February 2002 (serial number 10/083,200); MIT Internal Case 9558 (2002).

"Process for the Photocatalytic Production of Hydrogen from Protic Solutions using Two-Electron Mixed-valence Binuclear Complexes and Such Complexes"; PCT Int. Appl., (2003), pp 157.

"Optical Resonantor and Method of Making"; Preston Snee, Yin Thai Chan, Daniel G. Nocera and Moungi G. Bawendi; PCT Int. Appl. 60/631,427; MIT Internal Case 11424 (November 2004).

8. Honors/Awards

Italgas Prize 2005 (sometimes called the "Nobel Prize of Energy Research)

Elected to American Academy of Arts and Sciences, 2005

Sacconi Lecturer, University of Florence, 2005

Francis Clifford Phillips Lecturer, University of Pittsburgh, 2005

Emerson Lecturer, Georgia Institute of Technology, 2004